Development of polyvinylsilazane-derived ceramic matrix composites based on Tyranno SA3 fibers

Bernd MAINZER,† Martin FRIEB, Raouf JEMMALI and Dietmar KOCH

Institute of Structures and Design, German Aerospace Center (DLR), Pfaffenwaldring 38–40, 70569 Stuttgart, Germany

A damage tolerant weak matrix SiC fiber reinforced composite was developed by utilising a polyvinylsilazane in the polymer infiltration and pyrolysis (PIP) process. The polysilazane was infiltrated via resin transfer moulding in a layup of SA3 fabrics, thermally cured and pyrolyzed. This process was repeated until a residual open porosity of below 5% was reached. During pyrolysis the polyvinylsilazane converts to an amorphous SiCN matrix. In combination with the high modulus Tyrannon SA3 SiC fibers a weak matrix composite is created. To protect the composite in oxidative environment at high temperatures, an exterior SiC coating by means of chemical vapour deposition was applied. The polyvinylsilazane was investigated in terms of differential scanning calorimetry and measurement of viscosity to find the ideal temperatures for the polymer infiltration step. Specimens of the precursor were cured and pyrolyzed. The densification during pyrolysis was investigated in terms of He gas pycnometry and X-ray diffraction. The composite was characterized by SEM, μCT and mercury intrusion porosimetry. To determine the suitability of the SiC/SiCN composite for high temperature applications, samples were oxidized and tested by means of 3-point bending.

Key-words : SiC/SiCN, SiC/SiC, Ceramic matrix composites, PIP, Polysilazane

Fig. 1. Scheme of the PIP process.

1. Introduction

1.1 Silicon carbide fiber reinforced silicon carbide

SiC-fiber reinforced silicon carbide (SiC/SiC) is a trendsetting structural material which has recently found its way into mass production as components for the high temperature section of the LEAP jet engine.¹ SiC/SiC composites offer performance advantages such as higher temperature capability and significant lower density over the currently used metallic superalloys. A higher temperature capability allows reduced cooling air requirements and thereby improved fuel efficiency and reduced emissions.² Certain techniques can be used to manufacture SiC/SiC composites which can be distinguished by the way the composite’s matrix is generated. Typical techniques are reactive melt infiltration (RMI), chemical vapour infiltration (CVI) as well as polymer infiltration and pyrolysis (PIP).³

This work focusses on obtaining SiC fiber reinforced composites by the polymer infiltration and pyrolysis process (Fig. 1). It is a cycled two-stage process, beginning with the infiltration of a SiC fiber-preform with polymers. Instead of using polycarbo-silanes, a polysilazane was used. After thermal curing a following pyrolysis converts the polymer matrix to a ceramic SiCN matrix. SiCN ceramics are non-oxide ceramics with high thermal and chemical stability. During pyrolysis at low temperatures an amorphous, single-phase Si–C–N network is formed. Amorphous SiCN ceramics have been reported excellent high-temperature oxidation and creep resistance.⁴⁻⁵ These properties in combination with low densities make such ceramics a promising material for gas turbine applications, especially for rotating parts such as turbine blades.

Resin transfer moulding was used as a production technique, allowing a homogeneous infiltration of resins as well as controlling temperature and pressure during the curing process, which results in a dense SiC fiber-reinforced polymer (SiCFRP). A resin with low viscosity is favourable for good infiltration results. The followed pyrolysis converts the polymer matrix to a SiCN ceramic matrix. During pyrolysis the matrix shrinks due to the evaporation of volatile compounds and due to an increase of the density. The embedded fibers prevent the shrinkage of the whole composite. The shrinkage is compensated by the evolu-

©2016 The Ceramic Society of Japan All rights reserved.

DOI http://dx.doi.org/10.2109/jcersj2.124.P10-1

Fig. 1. Scheme of the PIP process.

for gas turbine applications, especially for rotating parts such as turbine blades.

Resin transfer moulding was used as a production technique, allowing a homogeneous infiltration of resins as well as controlling temperature and pressure during the curing process, which results in a dense SiC fiber-reinforced polymer (SiCFRP). A resin with low viscosity is favourable for good infiltration results. The followed pyrolysis converts the polymer matrix to a SiCN ceramic matrix. During pyrolysis the matrix shrinks due to the evaporation of volatile compounds and due to an increase of the density. The embedded fibers prevent the shrinkage of the whole composite. The shrinkage is compensated by the evolu-

Corresponding author: B. Mainzer; E-mail: bernd.mainzer@ dlr.de

Dedicated to Prof. Ralf Riedel on the occasion of his 60th birthday

Preface for this article: DOI http://dx.doi.org/10.2109/jcersj2.124.P10-1

DOI http://dx.doi.org/10.2109/jcersj2.16107
low specific surface and therefore the oxidation resistance is increased. Infiltration and pyrolysis is repeated until a desired residual porosity of below 5 vol-% is achieved. SiC/SiCN composites with 33% fiber volume content based on pyrolytic carbon coated Tyranno SA3 fibers (Ube Industries Ltd., Japan) have shown an average bending strength of 285 MPa but lacked of stability at high temperatures against oxidation.\(^{21}\) It was shown that the carbon coating was completely oxidized after 20 h at 1100°C in ambient air, resulting in a gap between fiber and matrix. A following passive oxidation partly converted the SiC fibers as well as the SiCN matrix to SiO\(_2\). The average strength was reduced to 87 MPa, revealing that either an additional environmental barrier coating or an oxidation resistant fiber coating is mandatory. This work focuses on the manufacture, characterization and mechanical testing of comparable Tyranno SA3 based SiC/SiCN composites with increased oxidation resistance. This is achieved by avoiding a fiber coating and relying on the creation of a weak matrix composite and by applying an additional CVD-SiC environmental barrier coating.

2. Experimental procedure

2.1 Characterisation of the precursor

A polyvinylsilazane (PSZ20, Clarient SE, Germany) was chosen as precursor for the matrix of the ceramic matrix composite:

\[
\begin{align*}
\text{CH}_2 & \quad \text{H} \\
\text{Si} & \quad \text{N} \\
\text{CH}_2 & \quad \text{H}
\end{align*}
\]

To determine the best temperature for infiltration during resin transfer moulding, the precursor was investigated in terms of curing and infiltration properties. The viscosity was measured in dry air by an oscillatory measurement with \(f = 10^{-3} \text{s}^{-1}\) in a plate/plate rheometer system from 25 to 300°C with 2 K/min heating rate (MCR302, Anton Paar GmbH, Austria). To simulate curing in the resin transfer moulding process differential scanning calorimetry was made in gold plated high pressure capsules (Netzsch DSC 404, Netzsch Gerätebau GmbH, Germany). The same temperature range and heating rate were chosen and pyrolysed in graphite crucible in air, resulting in a gap between the composite and ceramic matrix. A following passive oxidation partly converted the SiC matrix. A total of eight PIP cycles were made to decrease the porosity of the composite. The temperature of pyrolysis of the first five cycles was at 1000°C and that of the last three cycles at 1200°C. Finally a SiC/SiCN plate with the dimensions 290 × 190 × 3 mm was obtained.

2.2 Manufacturing of the composite

A total of twelve layers of Tyranno SA3 plain weave fabrics with the dimensions 300 × 200 mm were laid on top of one another and inserted into a mold. The polyvinylsilazane was infiltrated at 80°C by means of resin transfer moulding. After being fully infiltrated, the curing process was realized at 260°C in a nitrogen atmosphere with a pressure of 20 bar. The composite was afterwards pyrolyzed in a nitrogen atmosphere at 1000°C with a pressure of 1 bar to convert the polymeric matrix to SiCN matrix. A total of eight PIP cycles were made to decrease the porosity of the composite. The temperature of pyrolysis of the first five cycles was at 1000°C and that of the last three cycles at 1200°C. Finally a SiC/SiCN plate with the dimensions 290 × 190 × 3 mm was obtained.

2.3 Characterisation of the composite

The SiC/SiCN plate was investigated in terms of porosity via Archimedes water infiltration method. For a more detailed investigation of the porosity a small sample with ground surfaces and dimensions of 9.8 × 8 × 2.5 mm\(^3\) was prepared out of the lager plate. The sample was investigated via Archimedes method, followed by a micro-computed tomography (\(\mu CT\)) scan. This was performed using a high resolution \(\mu CT\)-System (nanotom, GE Sensing & Inspection Technologies GmbH, Germany) with a 12-bit flat panel detector with an active area of 2348 × 2348 pixels at 50 microns per pixel. The \(\mu CT\) scans were performed with the X-ray parameters 80 kV/180 \(\mu\)A at an exposure time of 1000 ms. A voxel size of 2\(\mu\)m could be achieved. The acquired X-ray images were reconstructed with a special algorithm known as Filtered Back Projection. The reconstructed volume was 3.5 × 3.5 × 2.5 mm\(^3\). The 3D image processing (visualization and calculations) was performed using VGStudioMax 2.2 (Volume Graphics GmbH, Germany) and Avizo Fire 9 (FEI SAS, France). As sample holder a rod made of borosilicate glass with a diameter of 3 mm was used. A cyanoacrylate superglue (CN, preusser-messtechnik GmbH, Germany) was used to fix the specimen to the glass rod. To avoid the infiltration of the pore network with the low viscosity CN and consequently wrong results, the bottom of the specimen was sealed with a two component adhesive (X60, HBW, Germany).

To determine the pore size distribution of the sample, mercury intrusion porosimetry was chosen (Pascal 140/240, Thermo Scientific, Germany). The pressure range was 0–200 MPa. Pore sizes between 10 nm and 100 \(\mu\)m were determined. The pore sizes were calculated with a cylindrical pore shape model and an assumed contact angle of mercury of 140°.

To determine the bending strength of the composite a total of ten samples with dimensions of 60 × 10 × 2.5 mm\(^3\) with ground surfaces were prepared. To improve the oxidation resistance of the composite the samples were completely coated with two layers of SiC with a total thickness of 70 \(\mu\)m by means of chemical vapour deposition. Five samples were oxidized for 20 h in ambient air at a temperature of 1100°C. The nonoxidized and oxidized samples were tested via 3-point bending test (according to DIN EN 658-3). The Young’s modulus was determined by using strain gauges. SEM images were made from the composites surface and polished cross sections of fiber bundles with the In-Lens detector with an acceleration voltage of 5 kV. The AsB detector was used for images of polished cross sections of the CVD-SiC coating with 12 kV and the SE detector was used for fracture surfaces with 5 kV (Zeiss Ultra Plus, Carl Zeiss NTS GmbH, Germany).
3. Results and discussion

3.1 Characterisation of the matrix precursor

The viscosity was measured in dependence of temperature with a heating rate of 2 K/min (Fig. 2). At 25°C the viscosity of the polyvinylsilazane was 0.46 Pa·s and decreased at higher temperatures to viscosities as low as 0.16 Pa·s at 98°C. Above 105°C the viscosity increased rapidly by cross-linking of the polyvinylsilazane. This behaviour was different from the DSC curve, showing an exothermal reaction beginning at 150°C with a maximum at 267°C. It is expected that the curing lead to a buildup of pressure in the high pressure capsules and thereby suppressed the cross-linking towards higher temperatures. Therefore for good curing results, the highest possible temperature in the resin transfer moulding device of 260°C was chosen for the manufacture of composites.

Figure 3 shows the diffractograms of the ground polysilazane pyrolysed at temperatures from 1100 to 1700°C. With increasing temperature the ceramic converts from fully X-ray amorphous to a more and more crystalline composition of \( \text{Si}_3\text{N}_4 \) and \( \text{SiC} \). The polysilazane keeps X-ray amorphous at temperatures of up to 1500°C. Nevertheless, nanocrystalline phases cannot be precluded but are not detectable due to resolution limitations of X-ray diffraction. Above 1500°C the crystallisation of \( \text{Si}_3\text{N}_4 \) and \( \text{SiC} \) was detected. The intensities for \( \text{Si}_3\text{N}_4 \) and \( \text{SiC} \) reach a maximum at the highest chosen temperature.

With increasing crystallinity of the SiCN ceramics an increasing density was expected. Figure 4 shows the measured ceramic yields and densities of SiCN in dependence of temperature. All values are based on cured PSZ20 with a density of 1.14 g/cm³. Pyrolysed at 1100°C, the density was 2.25 g/cm³ and increased to the maximum temperature of 1700°C with a density of 3.17 g/cm³. From 1100 to 1400°C the increase in density is rather low. Above 1500°C the density increases considerably faster due to the crystallisation of \( \text{SiC} \) and \( \text{Si}_3\text{N}_4 \). The measured density at 1700°C was close to pure \( \text{SiC} \) (3.21 g/cm³) and \( \text{Si}_3\text{N}_4 \) (3.18 g/cm³). An overview of the measurements is given in Table 1. For the cycled PIP process a low increase in density from polymer to ceramic is favourable. A high density of the SiCN matrix results in low volume yield and therefore a high amount of porosity within the composite. This will in turn lead to more infiltration cycles to reach the desired residual porosity of below 5 vol-% in the composite. At highest investigated temperature the volume yield was only 21.9% which is nearly half of the volume yield at 1100°C. Considering economy, as few as possible infiltration cycles are favorable. Nevertheless, to create composites for applications at temperatures of up to 1200°C, a maximum temperature of 1200°C for the PIP process was chosen.

After eight PIP cycles the SiC/SiCN plate was finished. Archimedes water infiltration showed a residual open porosity of 4.3 vol-%. The adjusted fiber volume content within the composite was 33%.

3.2 Investigation of the pore structures

For a more detailed investigation of the porosity a small sample with dimensions of 9.8 × 8 × 2.5 mm³ was prepared. The sample was measured with an open porosity of 4.8% and a true density of 2.46 g/cm³. Nevertheless, the Archimedes measure-

![Fig. 2. Viscosity and DSC curve of the PSZ20 polyvinylsilazane between 25 and 300°C.](image)

![Fig. 3. X-ray diffraction measurements of PSZ20 samples pyrolysed at different temperatures in nitrogen atmosphere for 10h.](image)

![Fig. 4. Mass yield and density of PSZ20 samples pyrolysed at different temperatures in nitrogen atmosphere for 10h.](image)

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Density [g/cm³]</th>
<th>Mass Yield [%]</th>
<th>Vol. Yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>260</td>
<td>1.14 ± 0.01</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>1100</td>
<td>2.25 ± 0.02</td>
<td>77.9</td>
<td>39.7</td>
</tr>
<tr>
<td>1200</td>
<td>2.27 ± 0.01</td>
<td>77.0</td>
<td>38.8</td>
</tr>
<tr>
<td>1300</td>
<td>2.29 ± 0.01</td>
<td>76.1</td>
<td>38.0</td>
</tr>
<tr>
<td>1400</td>
<td>2.34 ± 0.01</td>
<td>75.3</td>
<td>36.8</td>
</tr>
<tr>
<td>1500</td>
<td>2.48 ± 0.01</td>
<td>74.2</td>
<td>34.2</td>
</tr>
<tr>
<td>1600</td>
<td>3.12 ± 0.01</td>
<td>63.4</td>
<td>23.3</td>
</tr>
<tr>
<td>1700</td>
<td>3.17 ± 0.01</td>
<td>60.7</td>
<td>21.9</td>
</tr>
</tbody>
</table>
ment can be flawed for such small samples. The sample was dried and afterwards investigated by μCT. A nonlinear filter, the median filter was used to reduce the noise in the images: the grey value of each voxel is substituted by the grey value of the voxels in the neighbourhood. For further data analysis, it was necessary to classify the volume pixels either in void or solid. This step is called segmentation. There are several global and local segmentation algorithms in the literature. For the SiC/SiCN sample the Otsu’s threshold method was used for mainly two reasons. First, it is suitable for data sets with bimodal grey value distributions. Second, it is user independent, since it is based on statistical calculations. The result of the segmentation is a binary volume. A global 3D pore representation (surface rendering) is shown in Fig. 5(a). The scan revealed that the main porosity is located between the SiC fabrics in the matrix-rich regions of the composite [Figs. 5(b) and 5(c)]. Due to the strong ondulation of the plain weave SiC fabrics large matrix-rich volumes were found. The by far largest pores were detected outside of the fiber bundles in these matrix-rich volumes of the composite. The total detected porosity was 3.0 vol-% which is close to the measured Archimedes porosity. However, the value is lower due to resolution limitations.

The connectivity of the pore network in the SiC/SiCN material is assumed to be very high since pyrolysis leads to a shrinkage of the matrix therefore leading to cracks throughout the matrix. In order to prove this assumption, a labelling of the objects in a smaller region of interest (1 × 1 × 0.5 mm²) of the binary volume is performed [Fig. 6(a)]. Labelling is well known and very common image processing step: a label is assigned to each component. The result is a 3D representation in false colours [Fig. 6(b)] of separated regions, where different statistical data, such as volume and surface density are available. The different colours show cohesive porosity. However, in the CT volume data, not every pore was interconnected probably due to unsufficient resolution. Pores or cracks with a size below the voxel size 2 μm could not be determined.

To better describe and characterize the highly complex pore networks in the SiC/SiCN composite, the automatic skeletonization algorithm implemented in Avizo was used. The centreline of the porous networks was extracted from the image data. The result of the calculation was a spatial graph [Fig. 6(c)] consisting of 1602 nodes and 1763 branches, where nodes are connections and end points, and branches are the lines connecting the nodes. The distance-based skeleton or medial axis is a powerful tool to describe the fundamental geometry of complex three-dimensional geometries.

The pore size distribution was determined via mercury intrusion porosimetry. The SiC/SiCN composite shows a bimodal pore size distribution with a maximum at 8180 nm. The average pore diameter is 596 nm (Fig. 7). In total, a porosity of 3.53 vol-% was detected, which is between the measured values for Archimedes and μCT.

### 3.3 Mechanical properties

A total of ten samples were prepared for 3-point bending tests and equipped with an additional CVD-SiC coating with a thickness of 70 μm. The coating was applied in two cycles to prevent uncoated spots at attachment points. Thereof five samples were oxidized in dry air at 1100°C for 20 h (Fig. 8).

Figure 9 shows SEM images of the nonoxidized and oxidized composites. The matrix was dense within fiber bundles, having a shell-like structure. This is a result of the repeated PIP cycles by shrinkage and filling up of the evolved porosity. Large pores were found to exist outside of fiber bundles in matrix-rich areas of the composite.

The CVD-SiC coating had a crystalline morphology [Fig. 9(a)]. After oxidation the samples evolved SiO₂ on top of the SiC coating [Fig. 9(b)]. Nevertheless, the SiO₂ scale was so thin that it was not detected in SEM cross sections [Fig. 9(d)]. Besides of that the SEM images of oxidized samples were very similar in comparison to the nonoxidized samples. It was found that the second CVD-SiC layer did not attach properly to the first one, partially leaving a gap of about 1 μm in between.

The ten nonoxidized and oxidized samples were tested via 3-point bending. Although the manufactured composite had no
typical weak interface such as pyC or BN the damage behaviour was non-brittle. Two strength/strain curves of a nonoxidized and oxidized sample were selected for comparison (Fig. 10). The strain was measured with strain gauges. The unexposed samples had an average bending strength of 340 ± 20 MPa and strain rate of 0.4%. After oxidation the bending strength was 306 ± 56 MPa, which is a decrease of 10%. The strain rate was reduced to 0.36% which is a decrease of 10% as well. The Young’s modulus remained similar with 127 ± 19 GPa in comparison to 129 ± 7 GPa before oxidation. SEM images indicated that single fiber pullout was reduced after oxidation, leading to more block-like failure of whole fiber bundles. Fractured surfaces of unoxidized and oxidized samples are shown in Figs. 9(g) and 9(h). All samples failed on the tensile loaded side. Nevertheless the decrease is moderate in comparison to SiC/SiCN composites without environmental barrier coating. The strength of uncoated SiC/SiCN composites with pyC fiber coating, similar porosity and fiber volume content utilising the Tyranno SA3 fabrics decreased from an average 285 to 87 MPa.6)

The obtained SiC/SiCN composites in our case represent a weak matrix composite. Polymer derived SiCN ceramics have been reported to have rather low young’s moduli in the range of 82–140 GPa dependent from temperature during pyrolysis.11) In combination with the high modulus Tyranno SA3 SiC fibers with a modulus of 380 GPa12) a weak matrix composite is created. Therefore, propagating cracks were stopped or deflected by the reinforcing SA3 fibers, resulting in good fracture toughness. The concept of weak matrix composites is explained in more detail elsewhere.13)

4. Conclusion

A damage tolerant SiC/SiCN composite was manufactured without classical weak interface fiber coatings. Instead a polysilazane was utilised to create a weak matrix composite. Pyrolysis of the composite at 1200°C did create an amorphous SiCN matrix. Eight PIP cycles were used to densify the matrix to a low open porosity of below 5 vol-%. μCT scans revealed that the porosity is located mainly outside of fiber bundles within the SiCN matrix. A large amount of interconnected porosity was detected. The 70μm CVD-SiC environmental barrier coating was sufficient to prevent oxidation of the composite at the chosen conditions, resulting in an average bending strength of 306 MPa after oxidation in comparison to 340 MPa of the nonoxidized samples. The SiC coating certainly blocked the access of air into the vast porosity network and therefore helped to protect the composite against oxidation.
Fig. 9. SEM images of the CVD-SiC coated SiC/SiCN composite before (left column) and after oxidation (right column): (a and b) CVD-SiC surface; (c and d) cross section of CVD-SiC coating on composite; (e and f) cross section within the composite showing SiC-fibers in the SiCN matrix; (g and h) fractured surface showing fiber pullout.
XRD studies have demonstrated that pyrolyzed samples were amorphous at temperatures of up to 1500°C. Above this temperature SiC and Si$_3$N$_4$ were detected. The increase of density was moderate up to 1500°C and considerably higher at 1600 and 1700°C respectively. At 1700°C the density reached a maximum of 3.17 g/cm$^3$ which is close to the density of pure SiC and Si$_3$N$_4$.

In future research, the fiber volume content will be increased to possibly increase the strength of the SiC/SiCN composites. Furthermore, composites will be manufactured at elevated temperatures to increase the stability under conditions of use as well.

**Acknowledgements**  The financial support for the NewAccess project (03EK3544A) by the Bundesministerium für Bildung und Forschung is gratefully acknowledged. We also want to thank Ms. Noriko Metzger-Sata for performing the Hg-porosimetry measurement.

**References**

12) Ube Industries, Ltd., Tyranno Fiber®, product brochure.

![Fig. 10. Typical 3-point bending stress/strain curves of CVD-SiC coated SiC/SiCN composites before and after exposure to air (T = 1100°C, t = 20 h).](image)